REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
18-02-2015	Final Report	11-Feb-2014 - 10-Feb-2015

4. TITLE AND SUBTITLE
Final Report: X-Ray Diffraction for Research and Education in Southern Colorado

5a. CONTRACT NUMBER
W911NF-14-1-0065

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
206022

6. AUTHORS
Thomas M. Christensen

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
University of Colorado - Colorado Springs
CLEER
1420 Austin Bluffs Parkway
Colorado Springs, CO 80918 -3733

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
64724-MS-REP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
We examined three X-Ray Diffraction systems with an emphasis on thin film applications and their utility in a multi-user environment. We inspected all three systems and communicated with users of each system to determine the strengths and weaknesses of each system. We purchased the Rigaku SmartLab system based on a unique in-plane arm which allows greater thin film analysis capabilities and the automatic component recognition and user guidance software which we feel will be important in a multi-user facility at a smaller institution like ours. The

15. SUBJECT TERMS
X-ray Diffraction

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
UU	UU	UU	UU		Thomas Christensen
					19b. TELEPHONE NUMBER 719-255-3063

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

Final Report: X-Ray Diffraction for Research and Education in Southern Colorado

ABSTRACT

We examined three X-Ray Diffraction systems with an emphasis on thin film applications and their utility in a multi-user environment. We inspected all three systems and communicated with users of each system to determine the strengths and weaknesses of each system. We purchased the Rigaku SmartLab system based on a unique in-plane arm which allows greater thin film analysis capabilities and the automatic component recognition and user guidance software which we feel will be important in a multi-user facility at a smaller institution like ours. The equipment was delivered and installed in November, 2014. Final training by the manufacturer was completed on February 5, 2015. The system has been tested with standard samples for thin film analysis, bulk analysis, powder analysis, small angle x-ray scattering, x-ray reflection, pole figures and reciprocal space mapping. The high temperature capabilities of the instrument were also used to examine the change in crystal structure of a Ba-Fe oxide film. We are currently performing research on a patterned Gd film sample, Cu thin films (75 nm) deposited on Si and SiO_2, and Ba-Fe oxide films.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

none

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Thomas M Christensen	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

none

X-Ray Diffraction for Research and Education in Southern Colorado
Thomas M. Christensen

Final Report: Scientific Progress and Accomplishments

This equipment grant was for the purchase of a versatile X-ray Diffraction (XRD) system for use at the University of Colorado in Colorado Springs. The equipment was received in November 2014 and the training was completed in early February, 2015. We purchased the Rigaku SmartLab system, shown in Figure 1, based on a unique in-plane arm which allows greater thin film analysis capabilities and the automatic component recognition and user guidance software which we feel will be important in a multi-user facility at a smaller institution like ours.

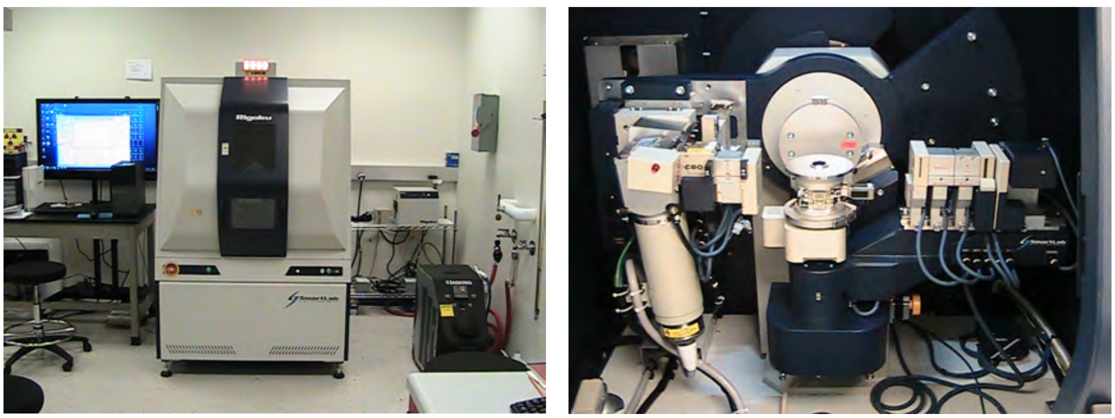

Figure 1. Rigaku SmartLab system and X-ray optics.

The capabilities of the system include Bragg-Brentano (focusing) and parallel beam geometries for the incident Cu X-rays. These two geometries can be changed by placement of slits in the optic path with no need to realign the incident optics. The instrument can be used for powder, bulk, and thin film samples. The system has been tested with standard samples for thin film analysis, grazing incidence diffraction, high-resolution diffraction, bulk analysis, powder analysis, small angle x-ray scattering, transmission diffraction, x-ray reflection, pole figures (texture analysis), stress analysis, and reciprocal space mapping. It also has a high-temperature stage capable of reaching 1500˚C in air, vacuum, or controlled atmospheres.

Given that this was an equipment grant, our scientific progress is from examining several samples in the last few weeks. We describe here some or these preliminary measurements and our plans for future projects.

We examined $BaFe_{12}O_{19}$ powder in order to be able to compare to films of $BaFe_{12}O_{19}$ which we prepare. Knowing the peaks and relative peak heights for a randomly oriented powder will assist us in understanding the orientation of our thin films.

The diffraction data for this powder, shown in Figure 2, agrees well with the data available in international databases. We performed a crystallite size analysis of the peak shapes, presented in Figure 3, and determined that the average crystallite size was 38 ± 7 nm and that the crystals did not show any strain.

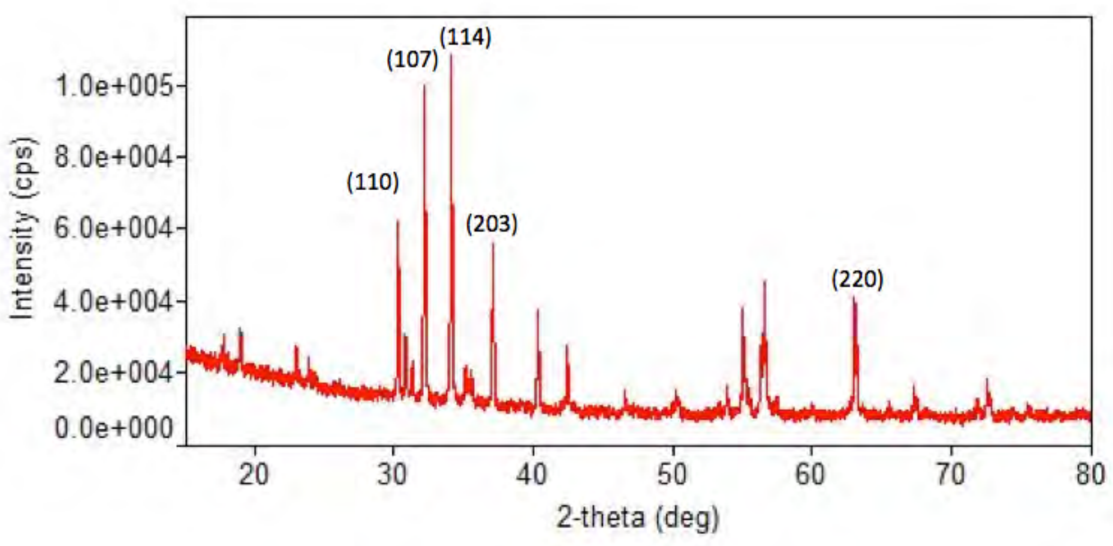

Figure 2. X-ray diffraction of $BaFe_{12}O_{19}$ powder

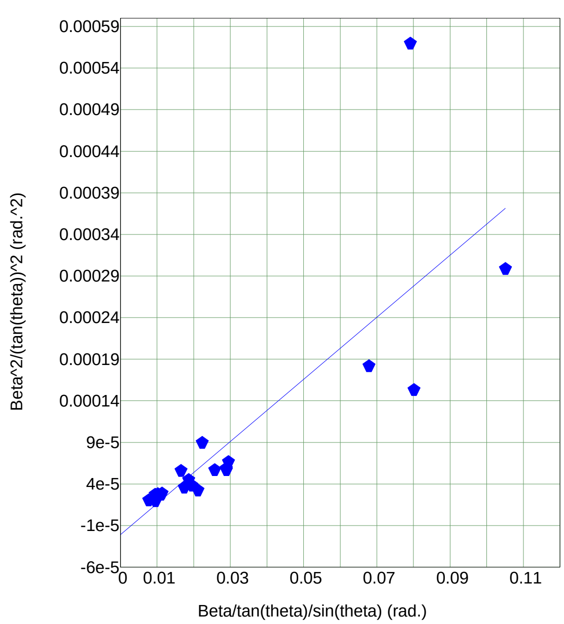

Figure3. Peak shape analysis for $BaFe_{12}O_{19}$ powder showing an average crystal size of 38 nm.

We examined a thin film of $BaFe_{12}O_{19}$ as well using grazing incidence XRD in order to suppress the Si substrate signal. The XRD data, shown if Figure 4, has peaks in the same positions as the powder but with a very different distribution of intensities. The (006) peak is very strongly enhanced and other peaks are significantly reduced indicating that the film grows with a preferred orientation.

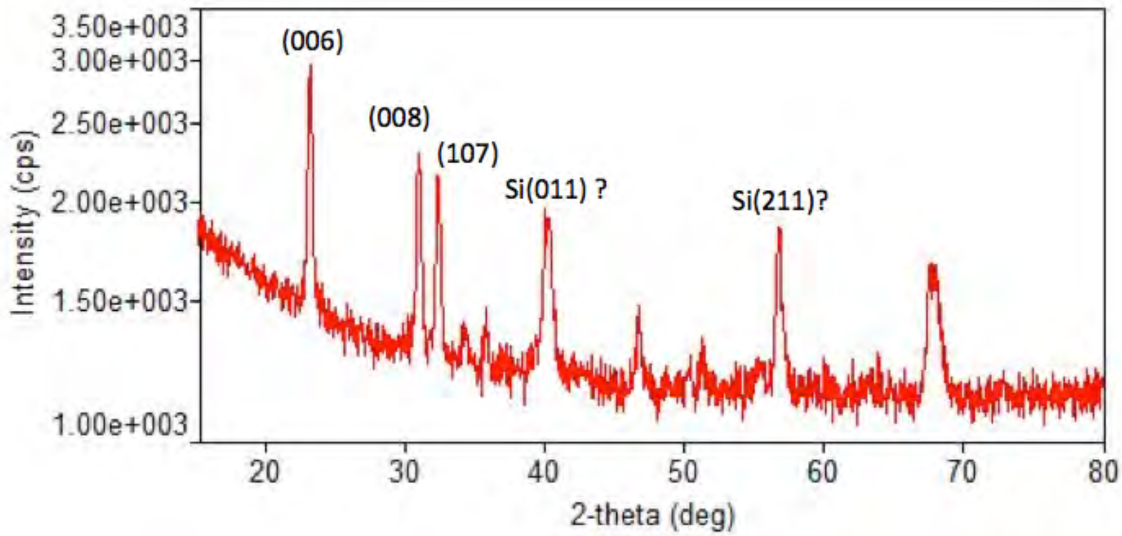

Figure 4. X-ray diffraction of $BaFe_{12}O_{19}$ film.

We examined a Ba-Fe oxide film in the high temperature stage at 500, 700, and 950˚C. The film was as-grown with no annealing. At the lowest temperature (500˚C), it showed minimal crystallization. At each higher temperature diffraction peaks began to appear and grew stronger at the highest temperature as the sample developed better crystalline structure as shown in Figure 5. Further experiments will characterize the crystallization process of these films in both air and nitrogen environments. These hexagonal ferrite films are particularly attractive as candidate materials for microwave devices operating above 35 GHz.

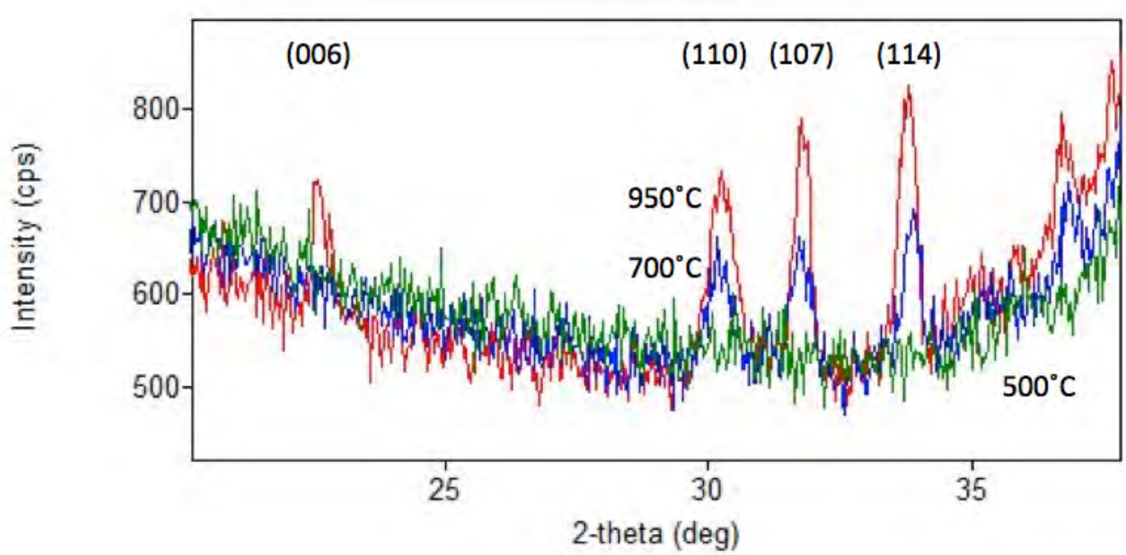

Figure 5. In situ annealing of Ba-Fe oxide film at three temperatures showing development of crystalline structure.

We examined Au nanoparticles both in water and evaporated out of solution. We performed small-angle X-ray scattering on the Au nanoparticles in solution. The signal quality, however, was weak due to the dilution of the particles. We intend to repeat these experiments with a less dilute particle solution and/or larger capillaries to increase signal strength. This will provide information about particle size. This work will be expanded to explore the behavior of noble metal nano-clusters and relate their structural properties to the optical and electronic properties.

The dried Au nanoparticles could be examined to determine crystallite size which may or may not be equivalent to the particle size discussed in the previous paragraph. Peak shape analysis of the Au nanoparticle X-ray diffraction spectrum indicates a crystallite size of about 44 ± 15 nm which was in good agreement with the expected result.

To better understand our thin film deposition processes and the effect of substrate on film properties we deposited 75 nm of Cu on both a Si substrate and 500 nm of SiO_2 on Si. Figure 6 shows that the XRD spectra of the two films are very similar in peak position, width and relative intensities. Figure 7 shows the X-ray reflectance on the two samples. More differences are seen here. Preliminary analysis suggests that the films have similar densities and roughness but somewhat different thicknesses.

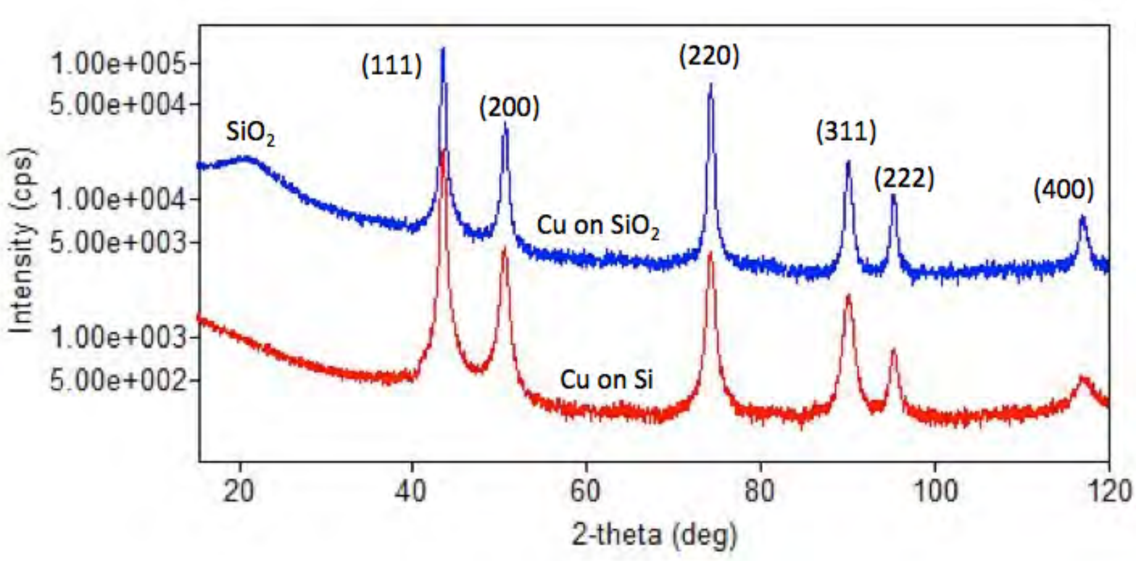

Figure 6. X-ray diffraction from Cu films on Si and on SiO_2. The spectra are shifted vertically for ease of comparison.

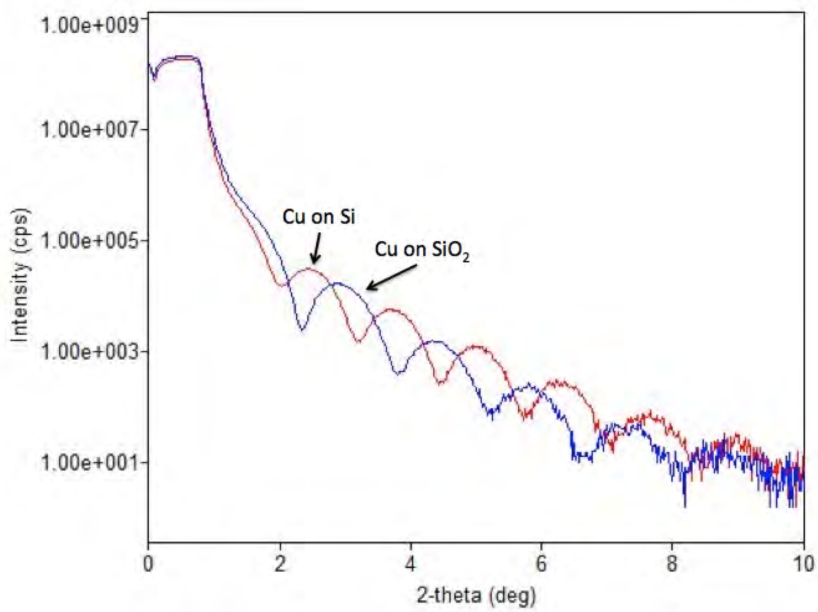

Figure 7. X-ray reflectance from Cu films on Si and on SiO_2.

In the future, we plan to examine films of Eu alloyed with 3d metals such as Mn, Fe, or Cr. These films, which can be grown using molecular beam epitaxy in our labs, are expected to display new phases under certain atomic ratios which have not been previously reported. The X-ray diffraction measurements are an important part of characterizing these films.

We also hope to examine enzyme and ligand interactions. These measurements, however, are typically done on dedicated instruments with higher intensity sources. We will explore whether we are able to get sufficiently strong signals by collecting data over long time periods.

The equipment clearly has great versatility. Five research groups are currently preparing samples for measurement on this equipment. It has expanded our capabilities significantly. We look forward to being able to correlate the structural information from XRD with our existing capabilities in magnetic, electrical, chemical, surface structure, and optical measurements.

On the education side, the equipment will be used in the graduate Solid State Laboratory class (PHYS 5150) this Spring. It will be an excellent opportunity to expose our students to this important characterization technique. We will incorporate the equipment into other classes and outreach opportunities in the future.